Mineralogical, Chemical and Morphological Variations among Analog Basaltic Lava Cave Speleothems  J. A. Ford¹, H. V. Kulkarni², A. Godet³, J. G. Blank¹, and S. Datta² Kansas State University, ³University of Texas at San Antonio, ¹Nasa Ames Research Center

Introduction: Basaltic caves at Lava Beds National Monument (LBNM), CA, offer a unique analog environment for potentially similar caves on Mars and other planetary bodies¹. In the presence of liquid water, caves at LBNM host diverse microbial communities and morphologically distinct secondary mineral deposits (speleothems) that could have formed via chemical or biochemical pathways. We investigate the potential pathways to discern between the biotic or abiotic mechanisms of speleothems formation using a combination of chemical, mineralogical and morphological techniques, which may serve to support future unmanned exploratory missions.

Methods: Speleothem samples (n = 100) and water samples (n=60) from 8 caves varying in physical factors (age of lava flow, visitation frequency, moisture content, temperature, light penetration) were collected and analyzed using conventional microscopy, x-ray diffraction (XRD), and fluorescence (XRF) to determine the mineralogical and elemental composition. A subset of 35 speleothem samples were also analyzed using a wavelength dispersive XRF spectrometer for validating the elemental data obtained with handheld XRF. Water samples, collected as droplets from lavacicles and puddles on cave floors, were analyzed using ion chromatography (IC) and ICP-OES for ionic and elemental composition. Dissolved organic carbon and nitrogen were quantified using a TOC/TN Analyzer.

Results and Interpretation: The host basalt consists of the following primary minerals: plagioclase, clinopyroxene, and olivine. A significant amount of speleothem samples were enriched in secondary minerals: cryptocrystalline silica (opal) and carbonates (Mg-calcite). Minor occurrences of hematite, magnetite, vanadium oxide, apatite, iron hydroxide were also detected in some samples and their concentrations were comparable to that in the basalt in the surrounding Medicine Lake.

Speleothem morphology, as described in prior cave studies², can largely be categorized as: Polyps (round bulb with short stem), Fingers (elongated), Coraloids (coral-like), Gours (flow-deposited / rimstone), and Encrustations (mineral crust on bare rock).

The samples that were dominated by the above primary minerals contain 42 – 50 wt% of SiO₂, while those enriched in secondary minerals contained up to 96 wt% SiO₂. Significant concentrations of biologically important elements (Ca, Mg, Fe, Mn, S, P, V) were detected in several speleothem samples. Other trace elements were also measured in elevated concentrations compared relatively to bare rock: Cu, Cr, Sr, Rb, and Ni. There appears to be a positive correlation between speleothem SiO₂ content and trace elements concentration. For example, some speleothems with high SiO₂ content (>80%) had excess of 1000 mg/kg Cu. Although the exact pathway of precipitation (biotic vs abiotic) is currently unknown for high SiO₂ speleothems, the precipitation process(es) are preferentially incorporating higher concentrations of the above elements as compared to the host rock and other basaltic features.

Thin sections of speleothem samples analyzed under both plane- and cross-polarized lights revealed micrometamorphic-like laminations. These laminae were composed of cryptocrystalline silica in some speleothem morphologies, similar to siliceous sinter deposits, while others contained laminae comprised of alternating calcite and cryptocrystalline silica. Moreover, the laminations of cryptocrystalline silica contain inclusions of glass fragments (as well as plagioclase, pyroxene, and clay fragments), indicative of the incorporation of volcanically produced fragments in a post-eruptive period in which the speleothems were in earlier stages of growth. Furthermore, the inclusions are most concentrated at the base and interior of the speleothem, which may suggest the inclusions in part acted as potential nucleation sites for further mineral growth.

The cave waters were found to be dominated by Si (23 ± 1 mg/L) followed by Na (8 ± 3 mg/L) and Ca (4 ± 2 mg/L) and varied within and among the caves. Elevated levels of NO₃⁻ (9 ± 8 mg/L) may be attributed to agriculturally influenced recharge or to in-situ microbial NH₄⁺ oxidation. Total P is also elevated (4 ± 1 mg/L). The cave waters also contained high concentrations of dissolved organic carbon (DOC, 13 ± 6 mg/L), which could support microbial growth. Composition of speleothems and cave water from the same location was found to be correlated. For example, high Ca²⁺ (7 ± 0.5 mg/L) was found in cave waters in the proximity of ~33% CaO carbonate polyp speleothems. P correlates strongly (R² = 0.91) with dissolved Si, possibly indicative of a phosphate precipitation associated with silicate dissolution within these secondary deposits.

Summary: Our results provide a link between the morphology, mineralogy, and elemental composition of speleothems alongside the water that interacts with these features in lava caves at LBNM. Findings of this study will help in determining the abiotic, biotic or combined pathways of speleothem formation. This
work is part of the NASA BRAILLE (Biologic and Resource Analog Investigations in Low-Light Environments) Project, an interdisciplinary PSTAR study of volcanic caves and associated biosignatures in preparation for possible future forays into similar resource-restricted environments on other planets, especially Mars.

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References: